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PATENT SPECIFICATION

NO DRAWINGS

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832,855

Date of filing Complete Specification Oct. 31, 1958.

Application Date Nov. 1, 1957. *No. 34145/57.*

Complete Specification Published April 13, 1960.

Index at acceptance:—**Class 2(3),** B4A4.

International Classification:—**C07d.**

COMPLETE SPECIFICATION

Catalytic Dehydrogenation of N-Methylpyrrolidine

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to catalytic dehydrogenation of N-methylpyrrolidine.

It is already known that the dehydrogenation of N-methylpyrrolidine can be effected in the vapour phase by treatment with hydrogen in the presence of a platinum or palladium catalyst. However, in such a process catalysts based upon metals of the platinum group have hitherto all proved to be extremely sensitive to poisoning so that their activity rapidly subsides.

We have now found that a particular form of platinum or palladium catalyst is outstandingly free from this serious disadvantage.

Thus according to the present invention we provide a process for the catalytic dehydrogenation of N-methylpyrrolidine to N-methylpyrrole by passing N-methylpyrrolidine vapour and hydrogen at elevated temperatures over a platinum or palladium catalyst characterised in that the catalyst is supported on silica gel.

The preparation of the catalyst to be used in the process of our invention may be performed in the manner already described in the prior art or in any other convenient manner. Thus the silica gel may be prepared by treating silica with dilute hydrochloric acid and washing and drying the gelatinous precipitate. Introduction of the platinum or palladium may be effected by impregnation of the silica gel with platinum or palladium chloride, for example by soaking the gel in a solution thereof in hydrochloric acid and reducing the chloride to the metal by means of hydrogen or formaldehyde and caustic soda. The amount of platinum or palladium introduced into the silica gel is conveniently from 1% to 10% of the weight of the gel.

The process of the invention is performed at elevated temperature of from 200—500° C., preferably from 300—400° C. In order to obtain maximum conversion of N-methylpyrrolidine to N-methylpyrrole with minimum production of condensation products and maximum catalyst life, the proportion of hydrogen in the gaseous mixture passed over the catalyst should be high, preferably at least 5 molecular proportions of hydrogen to 1 molecular proportion of N-methylpyrrolidine vapour. When lower proportions of hydrogen are used, increased quantities of high boiling by-products are formed and the catalyst is more readily poisoned. The proportion may with advantage be increased to 10 or more. The hydrogen issuing from the condensers may be recycled.

By the use of the catalysts according to the process of this invention N-methylpyrrolidine can be dehydrogenated to N-methylpyrrole with high conversion and high yield. The catalyst can be used for long periods without being poisoned. It can be readily regenerated as necessary by interrupting the flow of hydrogen and N-methylpyrrolidine vapour, sweeping out with nitrogen or other inert gas and passing air through with the furnace temperature unchanged until the rapid evolution of carbon dioxide ceases and the temperature of the catalyst falls again to that of the furnace.

The invention is illustrated but not limited by the following examples in which the parts and percentages are by weight.

EXAMPLE 1.

Silica gel, prepared from sodium silicate and hydrochloric acid, is extruded into pellets

and dried. 120 parts of the silica pellets are treated with a solution of an amount of hydrated palladium chloride equivalent to 6 parts of palladium in 15 parts of concentrated hydrochloric acid and sufficient water to ensure that whilst the whole solution is soaked up by the silica gel, the gel is fully saturated. The saturated gel is dried at 120° C. and cooled. It is heated to 100° C. under nitrogen and the temperature is gradually increased whilst hydrogen in increasing proportions is admitted to the stream of nitrogen passing through the mass. It is finally treated with pure hydrogen at 300° C. for 5 hours.

18 parts of silica gel containing 5% of palladium are placed in a heat-resistant glass tube surrounded by an electrically heated furnace. Hydrogen is passed through the tube at the rate of 0.2—0.25 parts per hour whilst the temperature is raised to 300° C. and maintained at 300±5° C. After 30 minutes at this temperature, the hydrogen flow is increased to 1.07 parts per hour and N-methylpyrrolidine vapour generated by dropping liquid N-methyl pyrrolidine at the rate of 8 parts per hour into the upper portion of the tube is introduced. The product is collected in cooled receivers. The conversion of N-methylpyrrolidine to N-methylpyrrole is 99.7% and the yield of N-methylpyrrole is 83%.

EXAMPLE 2.

18 parts of silica gel catalyst containing 5% of palladium prepared as in Example 1 are placed in a heat-resistant glass tube surrounded by an electrically heated furnace. Hydrogen at the rate of 0.2—0.25 parts per hour is passed through the tube while the temperature is raised to 250° C., and maintained at 245—255° C. After one hour the hydrogen flow is increased to 1.07 parts per hour and N-methylpyrrolidine is added at the rate of 4 parts per hour. This is vapourised in the upper part of the tube which is packed with beads and preheated to reaction temperature. The addition is continued for 14½ hours when the product is collected from the cooled receivers; 52 parts of product are obtained comprising 91 parts of N-methylpyrrole and 7% N-methylpyrrolidine. The yield of N-methylpyrrole is 91.2% and the conversion is 96.3%.

It is not necessary that the N-methylpyrrolidine used (for the reaction) should be pure. When made by certain methods N-methylpyrrolidine may contain water, with which it forms an azeotrope, and/or tetrahydrofuran. These substances are more easily separated from N-methylpyrrole than from N-methylpyrrolidine. It is therefore in these circumstances, an advantage to dehydrogenate the N-methylpyrrolidine in a mixture and then to separate the impurities, together with any by-products of the dehydrogenation reaction. The following example illustrates such a procedure.

EXAMPLE 3.

18 parts of a silica gel catalyst containing 5% of palladium prepared as in Example 1 are placed in a heat resistant glass tube surrounded by an electrically heated furnace. Hydrogen at the rate of 0.2—0.25 parts per hour is passed through the tube while the temperature is raised to 300° C. and maintained at 300±5° C. After 30 minutes at this temperature, the hydrogen flow is increased to 1.07 part per hour, and crude N-methyl-pyrrolidine containing 6% water and 7% tetrahydrofuran is added at the rate of 8 parts per hour. This is vaporised in the upper part of the tube which is packed with beads and preheated to reaction temperature. The product is collected in cooled receivers. from 153 parts of crude N-methylpyrrolidine, 137 parts of product are obtained, containing 103 parts of N-methylpyrrole, 10 parts of N-methylpyrrolidine, 8 parts of tetrahydrofuran, and traces of furan. The N-methylpyrrole is isolated in a substantially pure state by fractional distillation. The yield of N-methylpyrrole is 88% and the conversion 92.5%.

WHAT WE CLAIM IS:—

1. Process for the catalytic dehydrogenation of N-methylpyrrolidine to N-methylpyrrole by passing N-methyl-pyrrolidine vapour and hydrogen at elevated temperatures over a platinum or palladium catalyst characterised in that the catalyst is supported on silica gel.

2. Process for the catalytic dehydrogenation of N-methylpyrrolidine to N-methylpyrrole as claimed in Claim 1 wherein the amount of platinum or palladium introduced into the silica gel is between 1% and 10% of the weight of the gel.

3. Process for the catalytic dehydrogenation of N-methylpyrrolidine to N-methylpyrrole as claimed in Claim 1 or Claim 2 wherein the elevated temperatures used are from 200—500° C. and preferably from 300—400° C.

4. Process for the catalytic dehydrogenation of N-methylpyrrolidine to N-methylpyrrole as claimed in any of Claims 1—3 wherein the proportion of hydrogen in the gaseous mixture passed over the catalyst is high, preferably at least 5 molecular proportions of hydrogen to 1 molecular proportion of N-methylpyrrolidine vapour.

5. Process for the catalytic dehydrogenation of N-methylpyrrolidine to N-methylpyrrole as hereinbefore particularly described and ascertained especially with reference to the foregoing examples.

6. N-methylpyrrole whenever made by a process claimed in any of the preceding claims or by the obvious chemical equivalent thereof.

ALFRED O. BALL,
Agent for the Applicants.

PROVISIONAL SPECIFICATION

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EXAMPLE 2.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1960.
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